STUDY OF RHEOLOGICAL PROPERTIES OF GEL POLYMER ELECTROLYTE

Thesis Submitted for the Award of the Degree of

Master of Science

By

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DECLARATION

I hereby declared that the work presented in this thesis is carried out at **Department of Physics and Astronomy, National Institute of Technology, Rourkela**. I further declare that it has not formed the basis for the award of any degree, diploma or similar title of any other university or institution.

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CERTIFICATE

This is to certify that the thesis entitled, **"Study of Rheological Properties of Gel Polymer Electrolyte"** submitted by Srikanta Panda in partial fulfilment of the requirements for the award of Master of Science in Physics at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision.

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Iextend my truthful appreciations to my parents for their blessings, encouragement and moral support.

Srikanta Panda

DEDICATED TO MY

PARENTS

ABSTRACT

Two series of samples are prepared to investigate the viscoelastic properties of Gel Polymer Electrolytes. Samples were prepared by gelation techniquewith different oxygen to sodium ratio. For the present work, we take Poly(vinyliden fluoride) as polymer, sodium perchlorate as salt and of ethylene carbonate and propylene carbonate in the mass ratio of 1:1 and dimethylformamide as solvent for preparing the sample. X-ray diffraction analysis confirms the complexation of polymer with salt. The interplanar spacing and interchain separation of the gel polymer electrolytes were calculated from XRD data. The microstructurethe gel polymer electrolytes wereanalysedwith the help ofoptical microscopy. Viscoelastic properties and thermal stability of the sample were probed using rheological measurements.

CONTENTS

CHAPTER THREE

EXPERIMENTAL RESULTS AND DISCUSSION

CHAPTER FOUR

LIST OF FIGURES

LIST OF TABLES

ABBREVIATION USED

NAME	ABBREVIATION/ SYMBOLS
Amplitude Sweep	AS
Dimethylformamide	DMF
Ethylene Carbonate	EC
Gel Polymer Electrolyte	GPE
Inter Planar Spacing	d
Linear viscoelastic range	LVE
Loss Modulus	G”
Plasticized Polymer Electrolyte	PPE
Poly(acrylonitrile)	PAN
Poly(ethelene oxide)	PEO
Poly(methyl methacrylate)	PMMA
Poly(propylene oxide)	PPO
Poly(vinyl chloride)	PVC
Poly(vinyliden fluoride)	PVdF
Propylene Carbonate	PC
Shear Rate	$\dot{\gamma}$
Storage Modulus	G’
Strain	%
Temperature Sweep	TS
Viscosity	η

CHAPTER ONE

INTRODUCTION

In recent years extreme thrust has been given to develop high efficiency energy storage and conversion devices. One of the efficient energy conversion devicesis battery. The building blocks of batteries are electrodes and electrolyte.Though there are several disadvantages of using liquid electrolytes in batteries, still liquid electrolytes are used in most of the batteries because of its higher ionic conductivity. To overcome these limitations of liquid electrolytes research is in progress to find suitable alternative of liquid electrolytes. Use of solid electrolyte can be a probable solution but performance of the batteries made of solid electrolytes is not up to the desired level.A compromised approach has been taken here to replace the conventional electrolytes using gel electrolytes so that it can retain relatively high ionic conductivity values as of liquid electrolytes and at the same time maintain high mechanical stability as of solid electrolytes.

1.1 ORGANIZATION OF THESIS:

Chapter 1is the introduction part which gives the idea regarding basic of electrolysis process, electrolyte, role of polymer and salt in electrolyte, GPE and its impressive properties.

Chapter 2labels the procedure for synthesis of all polymer electrolytes in different salt concentration.

Chapter3 presents the characterization part in which all the possible measurable properties are discussed which include XRD characterization, Optical Microscopy and Rheologicalstudies.

Chapter 4 is the final part of this thesis which presents the summary and conclusions of the present work.

1.2 ELECTROLYTE

Electrolyte can be defined as the aqueous, molten and / solid substances in which electricity is conducted with the help of ions, in other words electrolytes are ionic conductors. Most common example of electrolyte is aqueous solution of common salt ($NaCl$).

Electrolytesthey can be broadly divided into two categories:

1. Liquid electrolyte
2. Solid electrolyte

Liquid electrolyte:

Liquid electrolytes are normally formed when salt is placed into a polar solvent and the constituent ions dissociate into positively and negatively charged ions due to the thermodynamic interactions between solvent and solute molecules, in a process called solvation.

Aqueous solution of sodium iodide (NaI) is a liquid electrolyte. In aqueous solution the constituent ions of NaI get dissociated into its constituent ions, which can be represented using the following equilibrium equation.

$$\boldsymbol{NaI \leftrightharpoons Na^{+} + I^{-}}$$

1.3 PROBLEMS WITH LIQUID ELECTROLYTE AND PROBABLE SOLUTION

The major benefit of using liquid electrolyte is in its high ionic conductivity. It makes it more suitable to be used in all the secondary energy conversion devices like lithium(Li) – ion batteries, Li metal hydride batteries,$Ni - Cd$batteries etc. [1]. But use of such liquid electrolytehas serious drawbacks, such as:

a. Limited temperature range for operation

In most of the batteries $LiPF_6$ based organic liquid electrolytes are used. It narrows down the temperature range of operation because liquid electrolytes are having a fixed boiling point and freezing point. The electrolyte cannot be used below and above the freezing point and boiling point respectively.

b. Leakage of electrolyte

Some batteries consist of harmful toxic chemicals and it may have threats of leakage because of its liquid state.

c. Bulky in size and low energy density

In general due to high mass density of liquid electrolytes, the batteries made of liquid electrolytes become heavy in weight hence the gravimetric energy density becomes less.

d. Corrosion of electrode materials

The liquid electrolytes are responsible for corrosion of cathode and anode by deposing uneven chemicals. It corrosion lowers the lifetime of the batteries.

e. Short life time

After power generation, it needs a longer time to stabilize the charge carrier and their duration or longevity is very less.

These are the major drawbacks due to which scientific community is looking for suitable alternatives and adopting the **solid electrolyte**as suitable substitute and trying to enhance its efficiency.

1.4 SOLID ELECTROLYTES AND THEIR CLASSIFICATION

The solids having high ionic conductive are called solid electrolyte. In general the conductivity of the electrolyte lies in between $10^{-6}$to $10^{-10}S/cm$range[2, 3].

To be useful solid electrolyte some essential features must be present, like;

a. It should have high ionic conductivity of the order $10^{-3}S/cm$ or higher
b. Low electron conductivity
c. Principal charge carrier must be ion
d. Low dissociation energy

Based on the mechanical and structural properties it can be classified in four different classes;framework polycrystalline materials, amorphous glassy electrolyte, Composite electrolyteand Polymer electrolyte.

If we look into ordering of these electrolytes, only frame work polycrystalline material is found to be ordered and the rest three are in disorder state [4].

1.5 ADVANTAGES WITH POLYMER ELECTROLYTES

The conventional polymer electrolytes i.e. polymer salt complexes are free from leakage and easily processable and they possess higher conductive properties as compared to other solid electrolytes. With respect to cost, size, safety, durability, and performance polymer electrolytes are by far the most beneficial than the other electrolytes.

1.6 POLYMER ELECTROLYTE AND THEIR CLASSIFICATION

To classify polymer electrolytes its physical properties and preparation techniques can be used as foundation for classification.

In a broad manner we can classify polymer electrolyte in fivedifferent categories.

a. Conventional polymer salt complex (PSC)
b. Plasticized polymer electrolyte (PPE)
c. Ceramic filler incorporated polymer salt complex (FBPE)
d. Ion conducting polyelectrolyte (ICP)
e. Gel polymer electrolyte (GPE)

The conductivity values of conventional polymer salt complexes are not up to the mark and required to be enhanced. In due course various methodologies have been adopted to increase the conductivity level at theexpense of losing its mechanical strength. One of the effective ways for increasing the conductive property of polymer electrolytes in general is to prepare gel polymer electrolytes.

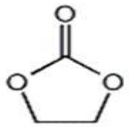
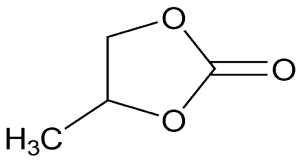
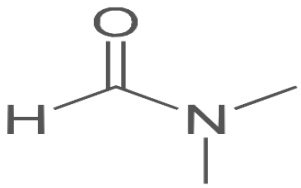
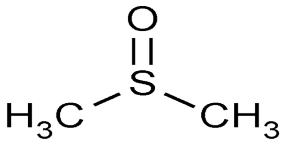
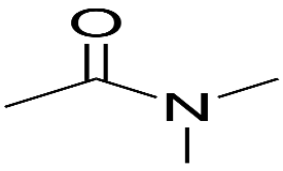
Gel Polymer Electrolyte

We define gel as the class of materials which behaves like **liquid**at microscopic level and **solid**in macroscopic state. As it behaves like liquid in microscopic level and solid in macroscopic level, hence the cohesive property of solid and diffusive property of liquid both coexist in gel polymer electrolyte.

Role of solvent, salt and filler in gel polymer electrolyte

Solvent has an important play in the gel polymer electrolytebecause it serves as the conductive medium.To increase the efficiency of the gel polymer electrolytes the solvents should have high dielectric constant so that it can aid the dissociation of dissolved salts, low viscosity and high boiling point. The elevated boiling point helps in maintaining the wide temperature range of operation of the electrolyte.

Table – 1.1 Comparative studies of different solvents

Solvent	M.P (°C)	B.P. (°C)	Viscosity (η)	Molecular formula	Structure
EC	38	244	1.90	$C_3H_4O_3$	
PC	– 55	240	2.53	$C_4H_6O_3$	
DMF	– 61	153	0.80	C_3H_7NO	
DMSO	18.4	189	1.1	C_2H_6OS	
DMA	– 20	165	1.93	C_4H_9NO	

Polymer gels are cage like substances having the capacity totrap the solvent inside it resulting in the increase of viscosity as well as its mechanical stability. For better result polymer should have high molecular weight, mechanical stability and low glass transition temperatureTg.

Salt is an indispensable part of the battery which when dissociates releases mobile ions which play a significant role in passage of current. It should have low dissociation energy (better dissolution) and bulky anions (to suppress dual ion conduction).

1.7 LITERATURE REVIEW:

C.B. Closs and his group demonstrated the rheological properties of aqueous starch system by adopting conventional strain sweep test which involves incremental increase in applied strain at a constant frequency (i.e. $0.02 - 0.5\ at\ 3.14\ rad/s$) and it was performed to determine the limits of the linear viscoelastic regions. Results of these tests were discussed in terms of storage and loss moduli [5].

Wei Yu and his co-workers used the rheological characterization to study the phase behaviour of partially miscible polymer blends. The temperature dependent storage moduli and tangent of phase angle for off critical blends and nearly critical blend are observed. Local maximum and inflection points were considered for further studies [6].

S. Ramesh studied the rheological characterization of ionic liquid based gel polymer electrolyte and studied the transitional behaviour by taking the oscillatory and amplitude sweep test,and found no transitional state (from solid to liquid). He found the elastic behaviour of the sample in the LVE range. He observed that the viscosity decreases with increase in shear rate for the reason of structural change [7].

Zhang *et al*. prepared PVdF blend film and studied the mechanical property. He compared the toughness of the film to check the tensile stress. They found that the mechanical property purely depend on the percentage of PVdF content in the sample. On the variation of composition he further studied the pore size and crystallinity of the same sample [8].

Triebel*et.al* investigated the temperature dependence of the zero shear viscosity. The angular frequency is compared as a function of creep time for PMMA. It matches with experimental

mode of observation. Other than that the thermo-rheological behaviour of storage modulus of the same material was observed[9].

A. K Elerkisand group take the PEO clay nanoparticles and studied the unusual rheological behaviour, like effect of molecular weight of the matrix, nature of surfactant, effect of temperature and conclude that at increase in temperature the nanoparticle have observable increase in viscoelastic property [10].

J. Kruckel and his group studied the rheological properties of PMMA/CB (carbon black) in which the storage modulus (G') of PMMA composite increases significantly at small angular frequencies. By increasing the carbon black filler in 2% of molar concentration, he analysed the behaviour of G' and observed the disappearance of Newtonian plateau at low frequencies while the viscosity increased for relative frequencies [11].

Paul steeman and his group studied the rheological and mechanical behaviour of a series of linear and randomly branched polyamide samples with varying molar mass and degree of moderate branch. It has been observed that chain branching had pronounced effect on the rheological behaviour of the material in both shear and extensional flow. Shear thinning and zero viscosity increases with branching. He also studied the mechanical property (deformation behaviour) by stress-strain measurement in tension. By incorporation of branches of adequate length, the melt strength (elongational flow) can be significantly enhanced [12].

M. Wang measured the shear viscosity as a function of shear rate for wt. %(0, 10, 20, 40, 80) of PMMA solution at room temperature and found that shear thinning behaviour of fluid at a low shear rate. By the help of extensional rheometer he studied the modulus of gel sample which helps to determine the dispersion stability of PMMA-montmorillonite (MMT) fiber [13].

Bryan A. Baker studied the mechanical properties of polyacrylic acid-co-polyacrylamide (pAAc/pAAm) and polyacrylate acid-co-polyacrylamide (pNaAc/pAAm) based hydrogels as a function of total polymer content. They characterize the hydrogel stiffness and frequency sweep are observed. By analysing the data it was seen that elastic modulus was significantly higher than loss modulus [14].

Guo-dong Kang and Yi-ming Cao studied the enhancement of thermal stability and other membrane properties for scientific and industrial purpose. He suggests the overview of PVdF membrane in terms of its modified properties. He applied his research on pollution control, lithium ion battery and more application. He also made the hydrophilic modification and used in applied science [15].

Varij Panwar*et al*. studied the dynamic chemical property of ionc polymer metallic composite (IPMC) by using the PVdF was observed. The storage modulus and phase angle with respect to frequency was calculated. On IPMC of different blends, the storage modulus of different blends ware compared. The band width of those polymer blends was also analysed [16].

Johnny N. Martins*et al*. investigated the structural PVdF nano composite by using the process of melt blending. Then the viscoelastic and stuructural properties were investigated. It was found that 5% nano composite contained sample shows largest value of crystallinity. By using X ray diffraction and FTIR, the structural property was observed. Storage modulus and viscosity were analysed for further study [17].

Takshi Kashiwagi investigated the viscoelastic properties by measuring the storage modulus (stiffness) and frequency dependence characterization of PMMA. At $200°C$ (high temperature) he studies different sample and measured the stability of different composites. Then he varified with different concentration of integrant chemicals (clay and carbon nanotube) [18].

Kopesy *et.al* take the acrylic polyhedral oligometic silsequioxane (POSS)- PMMA blends and studied the viscoelastic properties. At constant temperature of $170°C$ the modulus properties are studied. The degree of dispersion was characterized by wide angle X –ray diffraction (WAXD) and dynamic mechanical analysis (DMA). It has been concluded that POSS behaves like a plasticizer. Other than this the glass transition temperature and time temperature suspension was successfully employed [19].

Maio Du studied the rheological properties of Poly (methyl methacrylate) (PMMA)/ poly (styrene-co-acrylonitrile) (SAN) at low temperature. It was observed that slope of plotting in strong modulus and shear stress decreases at low frequency. He verified itfor different ratio of PMMA/SAN as $80/20$ and $60/40$ and studied the morphology for varying temperature [20].

1.8 OBJECTIVES

Work has progressed in the field of enhancing the conductivity level of the GPEs but the mechanical strength of the prepared materials are not well studied. In this thesis focus is on the detail studyof mechanical properties of GPEs.The objectives of this work is to study the structural and viscoelastic properties of synthesized Gel Polymer Electrolytes with different characterization techniques.

1.9 WORK CARRIED OUT

1) Different kinds of GPE samples were prepared using PVdF as polymer with two different kinds of solvents.
2) Samples were prepared with different salt concentrations.
3) Structural and micro structural properties were characterized using XRD and optical microscopic techniques.
4) The rheologicalcharacterization techniques, with amplitude sweep and temperature sweep was performed to analyse the viscoelastic behaviour of the synthesized GPEs.

CHAPTER 2

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

2.1 MATERIAL UNDER INVESTIGATION

We prepared the PVdF gel polymer electrolytes using two different solvent. The first series of GPEswere preparedusingDMF as solventwhile in the second series a combination of EC and PCwith a mass ratio of 1:1wastaken as the solvent. Sodium Perchlorate ($NaClO_4$)was taken in varying amounts to form the polymer salt complex.

A. Selection of Polymer

Many polymer hosts are used to synthesize GPEs. Some of them are listed below:

- Poly(ethelene oxide) – PEO
- Poly(propylene oxide) – PPO
- Poly(acrylonitrile) – PAN
- Poly(methyl methacrylate) – PMMA
- Poly(vinyl chloride) – PVC
- Poly(vinyliden fluoride) – PVdF

These polymersare having certain advantages as well as disadvantages over each other. To achieve the desiredproperties one needs to select the polymer carefully.

We chose PVdF over other polymers as it has the following required features:

a) It has low cohesive energy and exhibits high flexibility.
b) It has highmolecular weight and provides high mechanical, thermal and chemical stability.
c) PVdF has very good electrochemical property. It has very good self – lifeat room temperature.
d) It's swelling properties and film stability can be tuned.

The structure of PVdF is given below.

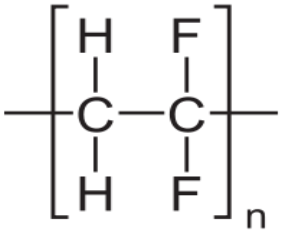


Fig 2.1 Structure of PVdF

B. Selection of Solvent

Combination of EC, PC (1:1 mass ratio) and DMF has been chosen as the solvents for preparing GPEs because of their high dielectric constant and high boiling point.

The structure of EC, PC, and DMF are given below.

(a) (b) (c)

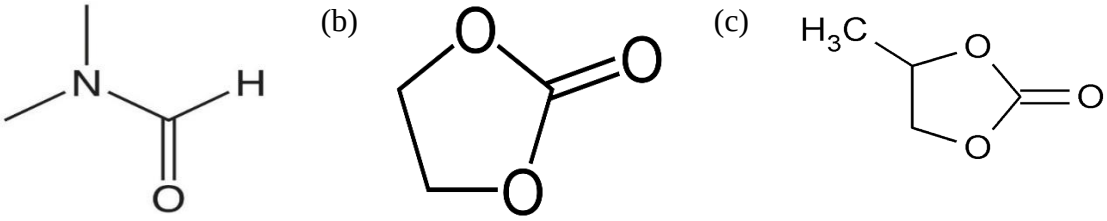


Fig 2.2 structure of (a) Dimethylformalamide (b) Ethylene carbonate (c) Propylene carbonate

C. Selection ofSalt

Sodium perchlorate ($NaClO_4$) has been chosen as the salt because of its low dissociation energy. Moreover the natural abundance of sodium makes this salt a possible substitution against highly reactive and hygroscopic lithium based salts.

Determination of O/Na ratio

Each samples having different salt concentration is expressed in form of O/Na ratio. This is the ratio between number of active oxygen in solvent and concentration of sodium atom in the salt. The ratio can be calculated by taking the relation i.e.

$$\frac{\mathbf{O}}{\mathbf{Na}} = \frac{\textbf{Mass of solvent}}{\boldsymbol{Molecular\ weight\ of\ solvent}} \times \frac{\textbf{Molecular weight of salt}}{\textbf{Mass of salt}} \times n$$

Where $'n'$ is the number of active oxygen

2.2 METHODS OF SYNTHESIS

Before going to synthesis it is very important to know the different way to synthesize the GPEs. There are many methods for preparing gel sample which include:

- Solution cast technique
- Hot press technique
- Gelationtechnique

For the present work gelation method has been used to synthesize all the samples.

2.3 SYNTHESIS OF POLYMER GEL ELECTROLYTE

The flow chart elucidating the preparation procedure of gel polymer electrolyte using different solventsare given below.

Synthesis of GPE using DMF as solvent

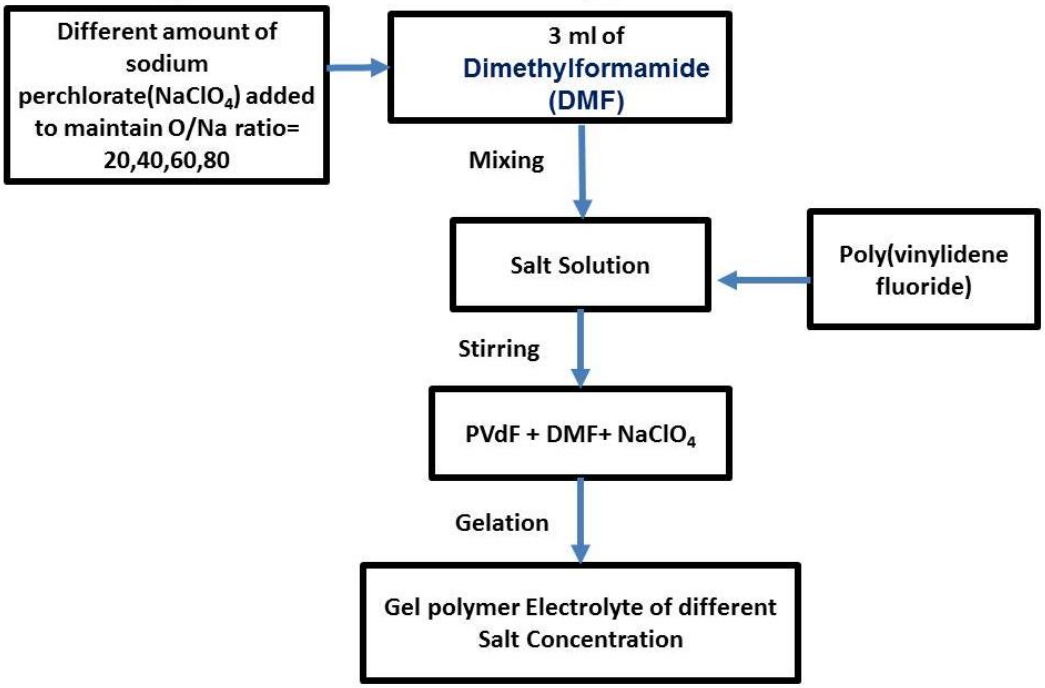


Fig 2.3 Procedure for synthesis of PVdF- EC+PC GPEs

Synthesis of GPE using mixture of EC PC as solvent

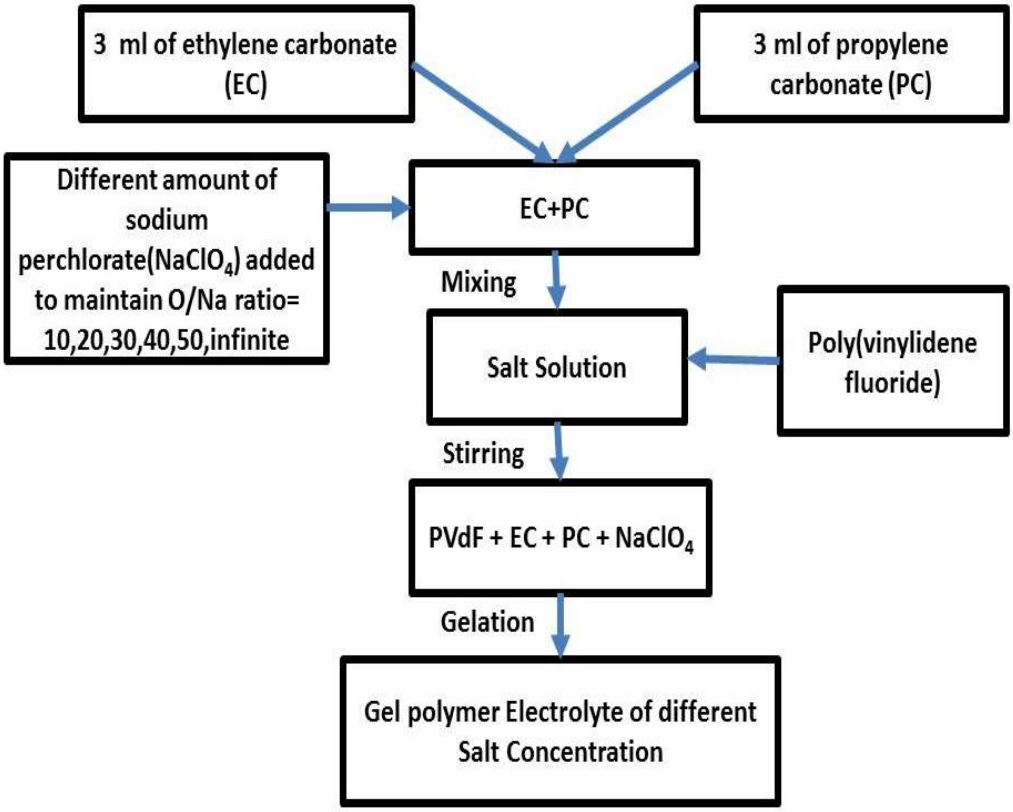


Fig 2.4 Procedure for synthesis of PVdF- DMF GPEs

2.4 EXPERIMENTAL TECHNIQUES USED

I. X – RAYDIFFRACTION

X – raydiffraction techniques gives information about the crystalline nature, interplanarspacing (d),chemical composition, interchainseparation (R) and physical properties of materials under investigation.The interaction of the incident rays with the sample produces constructive interference when conditions ofthe Bragg's law is satisfied

$$n\lambda = 2d\ Sin\ \theta.$$

Where,

n– order of diffraction ,λ– wave lengthof incident beam, d– interplannar spacing and, θ– angle of diffraction

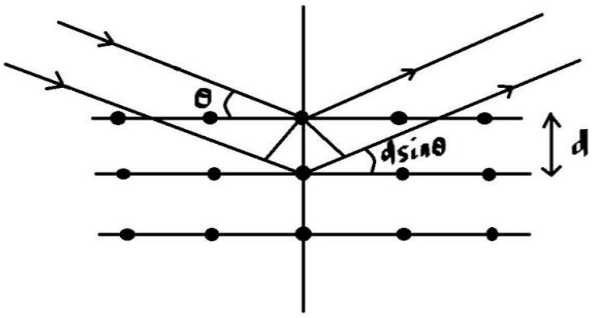


Fig 2.5 A typical diagram of Bragg's diffraction

From the obtained theta (θ) value we can calculate the interchain separation (R) for different sample using the following relation.

$$R = \frac{7}{2\pi}\frac{\lambda}{2sin\Theta}$$

Using Bragg's Law of diffraction 'inter planner spacing' can be calculated as

$$2d\ sin\Theta = \lambda \Rightarrow d = \frac{\lambda}{2sin\Theta}$$

Where symbols have their usual meaning.

II. OPTICAL MICROSCOPY

It is a type of microscope used visible light and an assembly of lenses are magnify images of the small sample. To study the surface morphology of the sample we have used optical microscopy. In this study we have used optical microscopy to observe the formation of cage like structure and their boundaries within GPE.

III. RHEOLOGY

Using rheological techniques mechanical properties of material can be determined. Rheology is used to find out the relationship between various observable parameter controlled by the mechanics of the material. It helps us to understand the relationship between the internal structural change and compositional variation with that of the applied external force.

- **Newton's Law of Viscosity (Gives the idea of ideal fluid)**

It state that,"Shear stress between adjacent fluid layers is proportional to the negative value of the velocity gradient between the two layers, where constant of proportionality is called coefficient of viscosity"[21].

- **Hooks law of Elasticity**

It states that, "If the deformation is small, the stress in a body is proportional to the corresponding strain [21]".Solids obeying Hook's law of elasticity are known as Hookean solids".

- **Viscoelastic behaviour**

All the materials we observe in nature do possess both solid like as well as liquid like properties up to a limited range of deformation. This superposition of elastic and viscous flow behaviour is called viscoelastic behaviour.

Rheological Measurements:

- **Amplitude Sweep (AS):**

Amplitude sweep is a type of oscillation test in which the amplitude of shear stress varies at a constant frequency and temperature. The plot between storage and loss modulus (G', G'')versus strain percentage furnishes the linear viscoelastic region which in turn gives the information about stability of the material. If $G' > G''$ is observed for a certain limit of deformation, we can say the elastic property dominates over the viscous property. And if loss modulus is has a greater value than storage modulus for a given value of deformation, then the material shows the viscous behaviour. The range of strain at which both G' and $G''$are parallel to each other; this is called linear viscoelastic (LVE).

- **Temperature Sweep (TS):**

Temperature sweep is generally used to find the critical temperature i.e. the point at which structure changes due to temperature. The plot between G' and G''against temperature gives the information regarding structural change of the sample. The temperature sweep also provides the information about the melting temperature of the gel samples. When we change

the temperature, the sample thinning property can also be verified. The information about the sample stability and performance can also be inferred from such measurements.

2.5 Instruments used for various characterizations

Table 2.1 Measuring instruments used for characterizing the samples

DIFFRACTOMETER
(make Rigaku)
Model # Ultima IV

Angle of diff. (θ): $-\ 5°\ to\ +$ 154°

Minimum-step
0.0001^{0}

speed
$0.01\ to\ 50^{0}/min$

radius
$285\ mm$

MICROSCOPE
(make Leica)
Model #DFC 295

Magnification-
$5\boldsymbol{X}\ to\ 100\boldsymbol{X}$

Focal
length$40\ to\ 2\ mm$

Resolution
up to $200nm$

RHEOMETER
(make Anton paar)
Model # MCR 102

Maximum torque
$200\ nm$

Pressure
upto $1000\ Pa$

Temperature
$-\ 5°C$ to $200°C$

Normal force
0.01 to 50

CHAPTER THREE

EXPERIMENTAL RESULTS AND DISCUSSION

3.1 X- RAY DIFFRACTION:

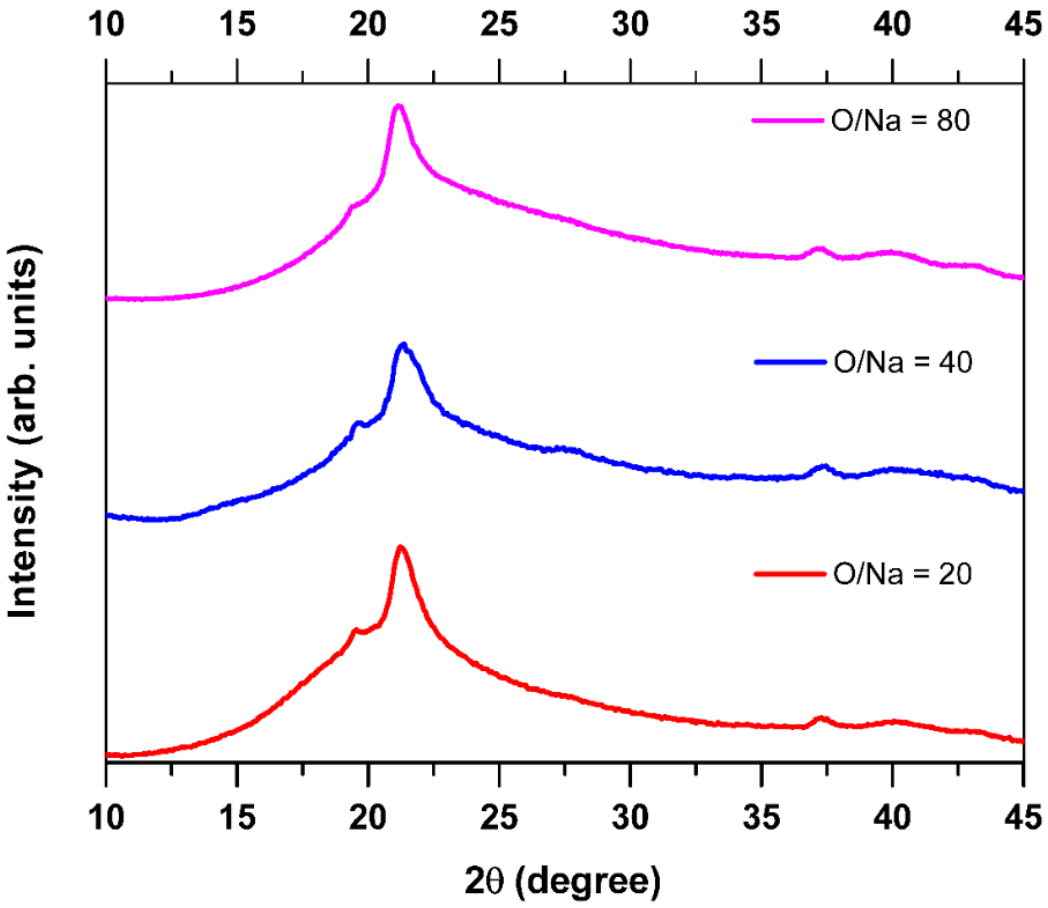


Fig.3.1 XRD patterns PVdF with DMF as solvent

The X-ray diffraction pattern are taken using Rigaku Ultima IV diffractometer with Cu K_α radiation ($\lambda = 1.5405$Å) for the angles ranging from 5° *to* 45°at the scan speed of $1°/min$. The XRD data shows a broad hump around 21°. We can conclude that the material PVdF-DMF gels are semi-crystalline in nature. It is noticed that when we increase the salt concentration, the position of the hump remains nearly unchanged. The interplanar spacing and interchain separations are calculated from the observed data and summarized in table 3.1.

Table 3.1 Interchain separation and Interplanar spacing of gel polymer electrolytes

O/Na	2θ (in °)	Interplanar spacing $d = \frac{\lambda}{2sin\theta}$(in Å)	Interchain separation $R = \frac{7}{2\pi}\frac{\lambda}{2sin\theta}$(in Å)
20	21.24	4.17	4.65
40	21.39	4.15	4.62
80	21.00	4.22	4.70

3.2 OPTICAL MICROSCOPY:

The surface morphology of the GPE samples at different magnifications were studied withLEICA DFC 295 optical microscope. Figure 3.2 shows the surface picture of PVdF gel added wtith DMF for O/Na = 40 sample.Optical microscopy shows a cage like structure of the polymer samples, which is in accordance to the existing understanding of gel samples.

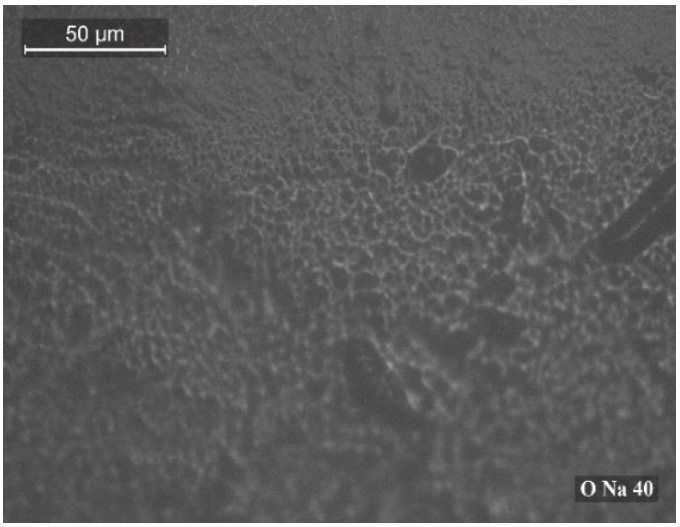


Fig. 3.2 Cage like structure of PVdF –DMF gel

The second gel sampleswere also studied to check the phenomenon of phase separation of GPEs. No significant conclusioncould be drawn from these figures as no clear indication of phase separation was seen. The samples looks uniformand nearly homogeneous.

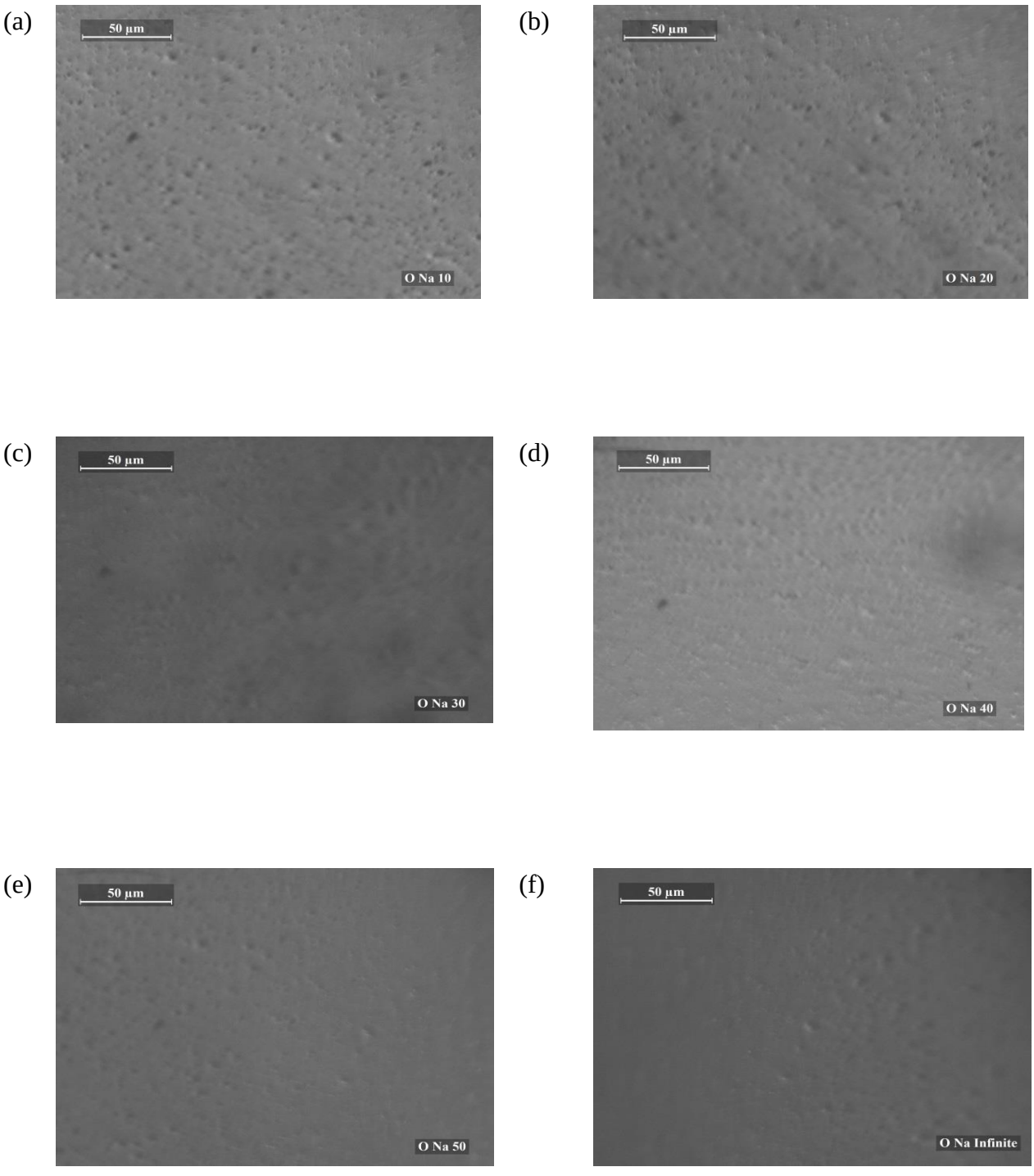


Fig 3.3 Optical microscopy of PVdF- EC,PC having O/Na ratio (a) 10, (b) 20, (c) 30 ,(d) 40 ,(e) 50, (f) infinite

3.3 RHELOGICAL ANALYSIS

I. PERTURBATION GIVEN AS AMPLITUDE

PVdF – DMFpolymer gel

The oscillation test i.e. amplitude sweep of PVdF – DMFgel with different salt concentration, O/Na= 20, 40, 60, 80 was done. Rheological characterizations were carried out using MCR 102 Rheometer (make Anton Paar) equipped with PP25 probe. The distance between upper surface of the sample and lower surface of PP25 probewasvaried according to the thickness of the sample.Strain percentage was kept between $0.01\ to\ 5\%$.The storage and loss modulus were measured at a constant temperature of $20°C$ and $10\ rad/s$ frequency.

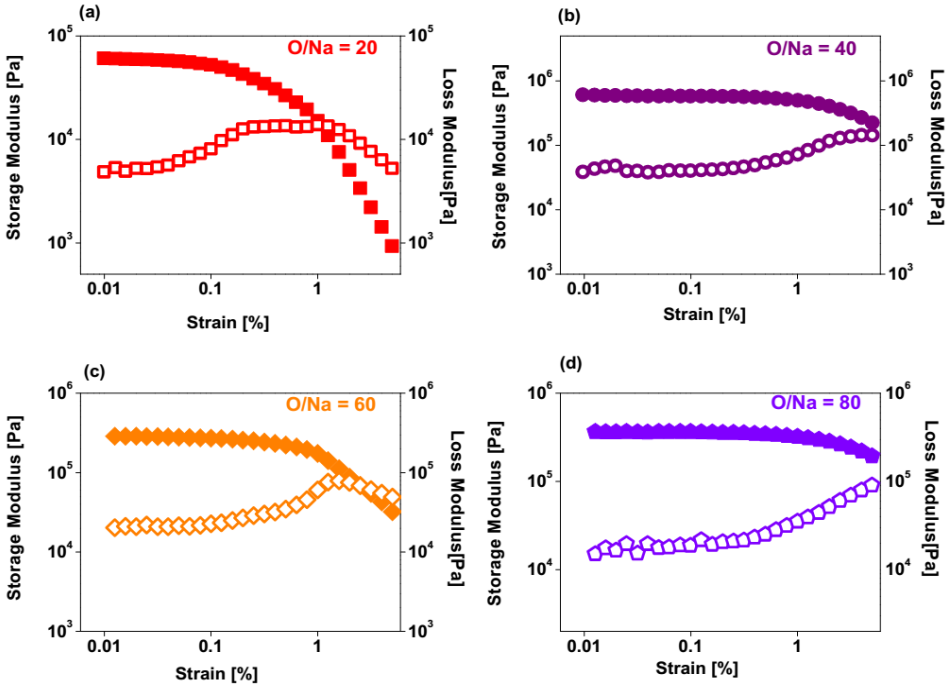


Fig 3.4 Amplitude sweep measurement of PVdF – DMF gels. Solid and open symbol represent the storage and loss modulus respectively.

Figure 3.4 shows the range of viscoelastic properties of the gel as a function of strain. It is observed that the storage modulus is constant over small strain change and at a particular strain decreases non – linearly with increasing strain. This could be due to breaking of weak vanderwaal bond at higher deformation [22]. Loss modulus increases with increasing in strain. Below the crossover point the elastic properties dominate over viscous properties of

the sample and after critical strain value, it reverses. Upto the crossover strain the sample is stable and shows an elastic behavior.

PVdF – EC,PC polymer gel:

The rheological measurements for the second sample with different salt concentration was also carried out. Measuring distance between probe PP25 and upper surface of the electrolytes was vaied between $1.2\ to\ 1.5\ mm$. Inthis casewe varied thestrain percent between $0.01\ to\ 50\%$.The storage and loss modulus were measured at a constant temperature, $20°C$ and with $10\ rad/s$ frequency.

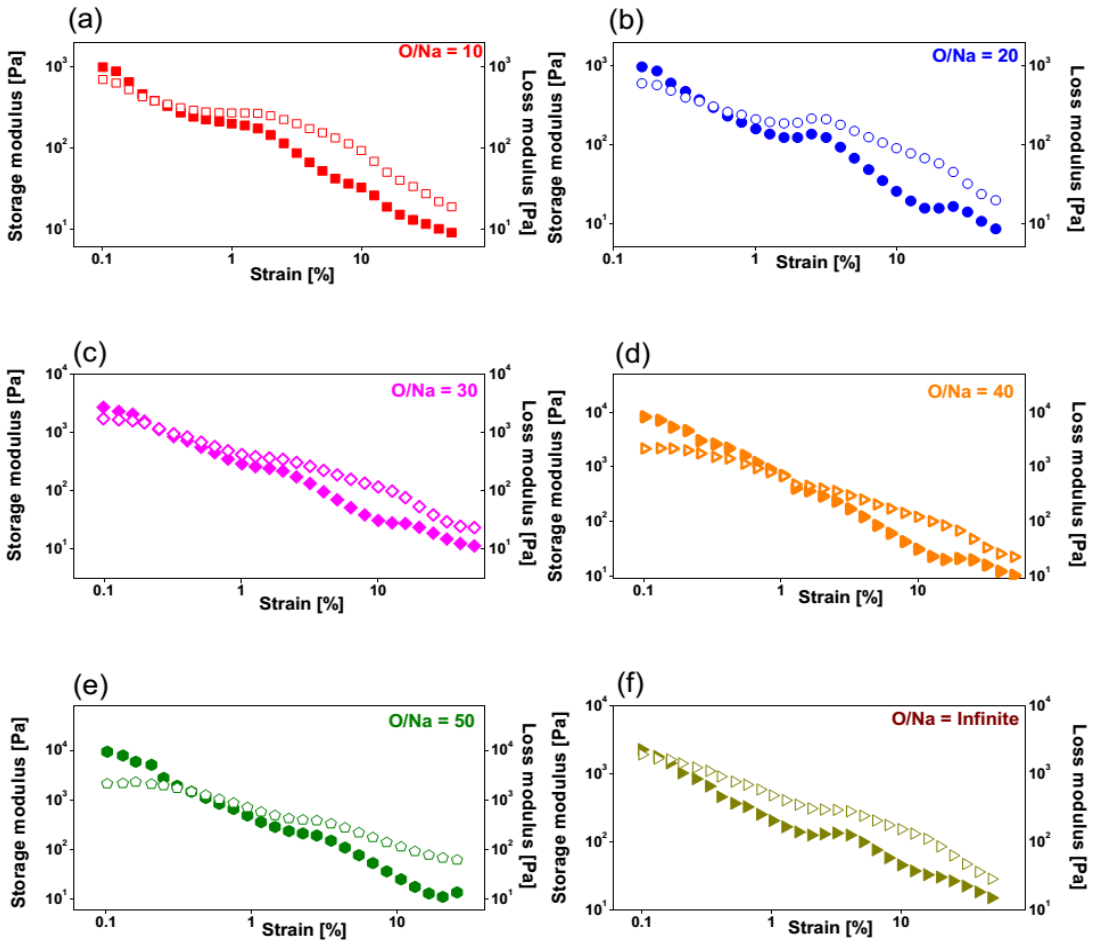


Fig 3.5 Amplitude sweep measurement of PVdF –EC+ PC gels . Solid and open symbol represent the storage and loss modulus respectively

From the curve we infer that G', G'' as a function of strain doesnot show appreciable linear viscoelastic range (LVR) indicating a lower stability than that of PVdF DMF sample. Among

these six different samples, in O/Na =40 shows the maximumcross over point at the strain value of 1.073%.

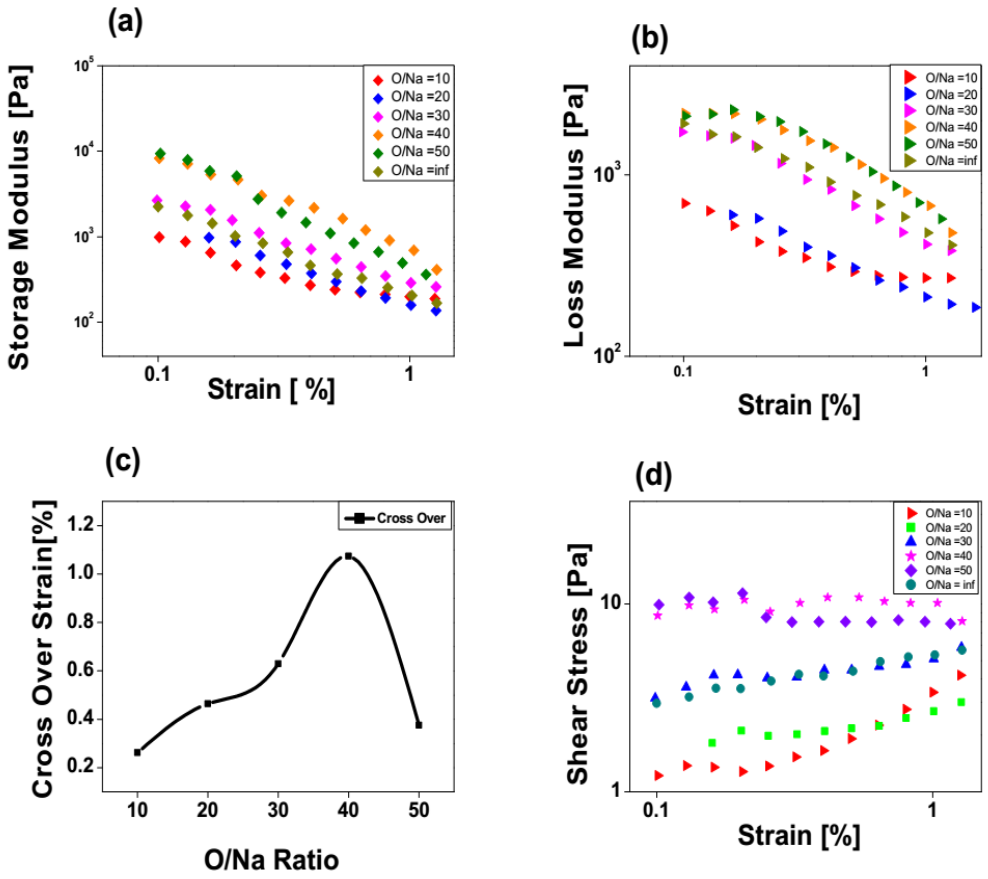


Fig 3.6 (a) G' vs. Strain, (b) G" vs. Strain, (c) Crossover Stain vs. O/Na ratio, (d)Shear stress vs. Strain. Solid and open symbol represent the storage and loss modulus respectively

Figure 3.6(c)shows a comparison between all the samples at crossover points with respect to different O/Na ratio. Figures 3.6 (a)and 3.6 (b), shows the *G'*and *G"*decreases with increase of strain which is in accordance to the literature. Overall we can conclude that for O/Na=40 sample exhibits a better stability compared to all other sample.

Table 3.2 O/Na ratio versus Cross over strain

PVdF–DMF	
O/Na Ratio	**CROSS OVER STRAIN[%]**
20	1.017
40	5.765
60	2.315
80	Falling outside the measurement range
PVdF – EC, PC	
O/Na Ratio	**CROSS OVER STRAIN[%]**
10	0.256
20	0.319
30	0.221
40	1.273
50	0.315
inf	0.141

II. PROBING THERMAL STABILITY

PVdF with DMF as solvent

The viscoelastic properties of PVdF– DMF were studied by varying the temperature from $10°C\ to\ 40°\ C$ with an increasing rate of $1°C/min$. The storage and loss modulus of the gel at different salt concentration against temperature are plotted in figure 3.7.

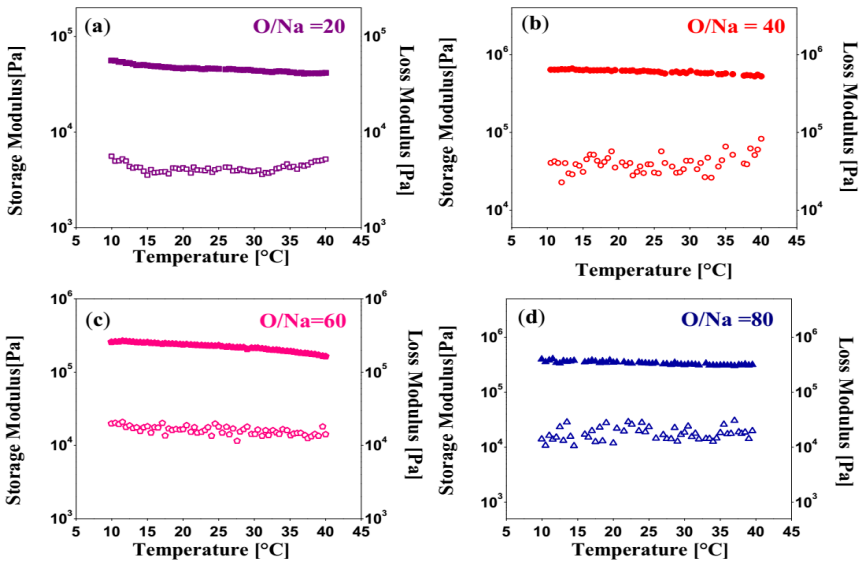


Fig 3.7 Temperature sweep measurement of PVdF EC+ PC gels. Solid and open symbol represent the storage and loss modulus respectively

The storage modulus decreases as temperature increases. This is a well studied effect which occurs due to weakening of bonding with increase in thermal fluctuation. It is found that storage modulus is highest for (O/Na = 40). There is no indication of loss of elastic property in the PVdF – DMF sample indicating higher stability.

PVdF with EC+ PC as solvent

The storage and loss modulus as a function of temperature for PVdF in EC, PC at different salt concentration was recorded by the temperature sweep measurement. The temperature was increased from $0 - 30\ ^{\circ}C$ at a rate of $1^{\circ}C\ /min$. In this range storage and loss modulus were recorded and the graph between the two against temperature is plotted below in figure 3.8.

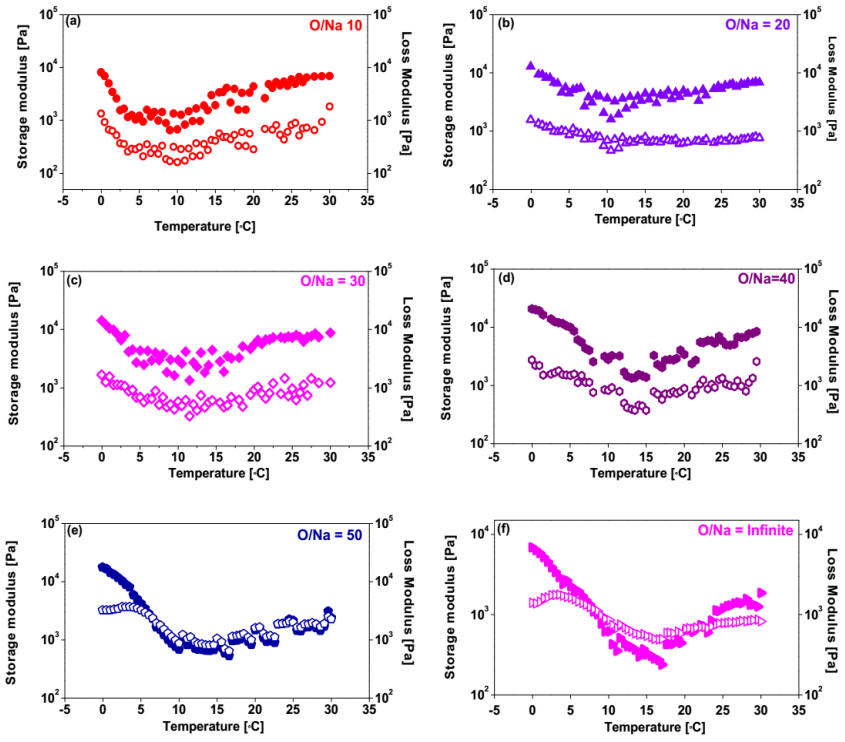


Fig 3.8 Temperature sweep measurementofPVdF – DMF gels. Solid and open symbol represent the storage and loss modulus respectively

From the plot it is clearly seen that storage modulus and loss modulus are overlapping in two samples O/Na= 50, O/Na=infinite (refer Fig 3.8 (e) and (f)). This observation suggests that this class of material is not suitable for the device fabrication purpose[23].

Table 3.3 Variation of G' and G'' with respect to temperature

VARIATION W.R.T G' AND G" WITH RESPECT TO TEMPERATURE.								
PVdF(DMF) GPE								
TEMPERATURE (In °C)	**O/Na=20**		**O/Na= 40**		**O/Na=60**		**O/Na=80**	
	G'[Pa]	**G"[Pa]**	**G'[Pa]**	**G"[Pa]**	**G'[Pa]**	**G"[Pa]**	**G'[Pa]**	**G"[Pa]**
10	55800	4960	640000	40700	628000	31100	400000	14100
20	46000	4210	621000	41200	621000	41200	350000	11900
30	43700	3880	616000	43200	616000	43200	328000	16900
40	41500	5190	525000	82800	525000	82800	319000	19800
PVdF(EC + PC) GPE								
TEMPERATURE (in $°C$)	**O/Na=10**		**O/Na= 20**		**O/Na=30**		**O/Na=40**		**O/Na=50**	
	G'[Pa	**G"[Pa]**	**G'[Pa]**	**G"[Pa]**	**G'[Pa]**	**G"[Pa]**	**G'[Pa]**	**G"[Pa]**	**G'[Pa]**	**G"[Pa]**
0	5050	672	9420	1340	10400	1560	19100	2200	14400	3250
10	675	164	3670	692	3010	579	2800	828	689	877
20	4410	285	4930	624	5550	926	3410	896	673	823
30	6930	1840	6900	762	8810	1230	2580	2580	664	816

CHAPTER – 4

4.1 CONCLUSIONS

From literature we found that the solid polymer electrolytes have low conductivity as compared to the conventional liquid electrolytes. Researchers have adopted different approaches to increase the level of conductivity including the incorporation of plasticizers and fillers to synthesis of gel polymer electrolytes. The gel polymer electrolytes exhibit both liquid like and solid like properties. Hence these materials can be tapped for the battery applications for their unusual properties.

We have synthesized the PVdF gel polymer electrolytes using different solvents DMF and EC+PC with variation of salt concentration to verify its mechanical and thermal stability. From our results we conclude that GPEs with DMF have a wider linear viscoelastic range as compared to the GPEs with EC+PC. Hence the PVdF – DMF samples exhibit higher elastic property up to a certain critical strain indicating higher mechanical stability which is acceptable. However for GPSs with EC+PC we found that the storage modulus increases initially but decreases later on for all the samples.

The temperature sweep results clearly indicate that PVdF – DMF samples exhibit an enhanced thermal stability over the PVdF – EC+PC samples. Hence we conclude that the PVdF – DMF samples are suitable for battery applications.

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